THE STABILIZATION OF SMOKELESS POWDER

MORTON ALVA PRAGER

Library
U. S. Naval Postgraduate School
Monterey, California

Mont 222
8854

The Stabilization of Smokeless Powder

A Thesis

Presented to the Faculty of the Graduate School of Cornell

University for the degree of

Master of Science in Engineering

By

Morton Alva Prager

June 21, 1946

Thesis
P6

Biography of Writer

The writer was born in Savannah, Georgia, on May 29, 1916. He attended public school in Savannah and West Palm Beach, Florida, and was graduated from the Alabama Polytechnic Institute in 1938, receiving the degree of Bachelor of Science in Chemical Engineering.

After graduation he was employed by the Southern Cement Company of Birmingham, Alabama, and Joseph E. Seagram and Sons, Inc., of Lawrenceburg, Indiana.

He was commissioned an Ensign in the United States Naval Reserve in 1942, and was on duty in Washington, D. C., for most of the late war, being promoted to Lieutenant in 1944.

7945

Geography of Indiana

Jim Walker was born in Greenwood, Indiana, on July 25, 1918. He attended public school in Greenwood and was Pain Lesson, Florida, and was graduated from the Indiana Polytechnic Institute in 1939, receiving the degree of Bachelor of Science in Chemical Engineering.

After graduation he was employed by the Southern Chemical Company of Birmingham, Alabama, and later by Dungan and Smith, Inc., of Indianapolis, Indiana.

He was commissioned an Ensign in the United States Naval Reserve in 1942, and was on duty in Washington, D. C., for most of the late war. He was promoted to Lieutenant in 1944.

The Stabilization of Smokeless Powder

Manufacture of Smokeless Powder

The smokeless powder used as a propellant in the armed forces of the United States is normally a "single-base" nitrocellulose powder made by colloidizing nitrocellulose containing about 12.6 per cent of nitrogen.

The nitrocellulose, known as "pyrocellulose", is made by nitrating either purified cotton linters or special alpha-cellulose prepared from spruce pulp. The material is nitrated in batches of about forty pounds each, with mixed acid of about the following composition:

	Per Cent
Sulfuric Acid	63
Nitric Acid	21
Water	16

A charge of almost 2000 pounds of acid is used for each batch of cellulose. The nitration usually takes about twenty-five minutes; the temperature of the acid being kept almost constant at 30-34° C. by cooling coils in the nitrator. The spent acids are then removed from the nitrocellulose by a centrifugal directly below the nitrator, and are fortified for reuse or sent to the recovery plant.

The partially dry nitrocellulose is forked through an opening in the center of the centrifuge into a trough containing a stream of water.

The drowned crude nitrocellulose contains some sulfate esters of cellulose, and some nitrate esters of oxycellulose

The Manufacture of Smokeless Powder

Manufacture of Smokeless Powder

The smokeless powder used as a propellant in the armed forces of the United States is normally a "single-base" nitrocellulose powder made by colloidizing nitrocellulose containing about 12.6 per cent of nitrogen.

The nitrocellulose, known as "pyrocellulose", is made by nitrating either purified cotton linters or special alpha-cellulose prepared from spruce pulp. The material is nitrated in batches of about forty pounds each, with mixed acid of about the following composition:

	Per Cent
Sulfuric Acid	63
Nitric Acid	21
Water	16

A charge of almost 2000 pounds of acid is used for each batch of cellulose. The nitration usually takes about twenty-five minutes; the temperature of the acid being kept almost constant at 30-34° C. by cooling coils in the nitrator. The spent acids are then removed from the nitrocellulose by a centrifugal directly below the nitrator, and are fortified for reuse or sent to the recovery plant.

The partially dry nitrocellulose is forced through an opening in the center of the centrifuge into a trough containing a stream of water.

The drowned crude nitrocellulose contains some sulfuric esters of cellulose, and some nitric esters of pyrocellulose

and of hydrocellulose; all of these impurities are less stable than nitrocellulose itself. They are all capable of being hydrolyzed by long boiling with slightly acidified water. To remove these impurities, the nitrocellulose is subjected to several stabilizing processes.

The first of these, known as "sour boiling", consists of a long series of boilings with water containing from 0.25 per cent to 0.50 per cent of sulfuric acid. The usual procedure is to boil a total of forty hours with at least four changes of water.

Even after the continued boiling, the fibers of nitrocellulose, which still have the hollow structure of the original cellulose fibers, usually retain some acid. To remove this acid, the fibers are "pulped". This is accomplished by a beater, a Jordan mill, or a combination of the two. Most of the acid contained in the fiber is released when the fibers are broken up, and is neutralized by a weak solution of sodium carbonate added during the pulping.

The pulped fibers still contain traces of adsorbed acid and of unhydrolyzed unstable esters; these are removed by "poaching". The pulp is boiled again repeatedly with dilute sodium carbonate and then with water, and finally is washed at least eight times by thorough agitation with water; each time at least 40 per cent of the liquid is decanted.

After washing, the material is screened to give finished pyrocellulose. If the pyrocellulose is to be converted

and of hydrous lignins; all of these impurities are less soluble than alpha-cellulose itself. They are all capable of being hydrolysed by long boiling with slightly acidified water. To remove these impurities, the alpha-cellulose is subjected to several alkalizing processes.

The first of these, known as "hot boiling", consists of a long series of boilings with water containing from 0.25 per cent to 0.50 per cent of sulphuric acid. The usual procedure is to boil a total of forty hours with at least four changes of water.

Even after the continued boiling, the fibres of nitrocellulose, which still have the hollow structure of the original cellulose fibres, usually retain some acid. To remove this acid, the fibres are "pulped". This is accomplished by a beater, a Jordan mill, or a combination of the two. Most of the acid contained in the fibre is released when the fibres are broken up, and is neutralized by a weak solution of sodium carbonate added during the pulping.

The pulped fibres still contain traces of adsorbed acid and of unhydrolysed unstable esters; these are removed by "poaching". The pulp is boiled again repeatedly with dilute sodium carbonate and then with water, and finally is washed at least eight times by thorough agitation with water; each time at least 40 per cent of the liquid is decanted.

After washing, the material is screened to give finished pyrocellulose. If the pyrocellulose is to be converted

to smokeless powder in the same establishment, it is pumped to the powder plant as a slurry. If it is to be shipped, it is dried to a water content of about 25 per cent and packed.

The first process in the actual conversion of pyrocellulose to smokeless powder is dehydration. The slurry is filtered by a continuous filter of the Oliver type and the pulp placed in a hydraulic press, where most of the water is removed by the application, for a short time, of a pressure of about 250 pounds per square inch. The pressure is released, and alcohol, in an amount at least equal to the dry weight of the nitrocellulose, is forced into the mass by a pump. The pressure is then increased to about 3500 pounds per square inch, pressing the material into a cylindrical block. The process is controlled so that the product retains just enough alcohol for the colloiding operation.

The compressed block is placed in a kneading machine and broken up by hand. This machine is similar to a bread kneading machine used in large bakeries. Then ether is added rapidly and mixed in as fast as possible. Enough ether is added so that the final liquid consists of about one part by weight of alcohol and two parts by weight of ether, the total weight of liquid being approximately equal to that of the nitrocellulose. The stabilizer is mixed with the ether before adding to the powder.

After mixing, the powder looks like brown sugar. It is soft enough to be deformed by hand, and sticks together when squeezed.

to nitrocellulose powder in the same establishments, it is passed to the powder plant as a slurry. If it is to be shipped, it is dried to a water content of about 25 per cent and packed.

The first process in the actual conversion of gunnitrocellulose to nitrocellulose powder is dehydration. The slurry is filtered by a continuous filter of the Oliver type and the pulp placed in a hydraulic press, where most of the water is removed by the application, for a short time, of a pressure of about 250 pounds per square inch. The pressure is released, and alcohol, in an amount at least equal to the dry weight of the nitrocellulose, is forced into the mass by a pump. The pressure is then increased to about 3500 pounds per square inch, pressing the material into a cylindrical block. The process is controlled so that the product retains just enough alcohol for the colloiding operation.

The compressed block is placed in a kneading machine and broken up by hand. This machine is similar to a bread kneading machine used in large bakeries. Then ether is added rapidly and mixed in as fast as possible. Enough ether is added so that the final liquid consists of about one part by weight of alcohol and two parts by weight of ether, the total weight of liquid being approximately equal to that of the nitrocellulose. The stabilizer is mixed with the ether before adding to the powder.

After mixing, the powder looks like brown sugar. It is soft enough to be deformed by hand, and sticks together when squeezed.

The incompletely colloidized material from the mixer is pressed into a compact cylindrical mass in a preliminary or "blocking" press, which exerts a pressure of about 3500 pounds per square inch. This block is then placed in a "macaroni press", from which it is forced through several small holes, to emerge as strings that look like macaroni.

These strings are placed in a final blocking press, which may be the same press used for preliminary blocking, and reformed into a cylinder. In this operation the pressure is maintained for one or two minutes; this application of pressure completes the colloiding.

The block from the final press is placed into the graining press, from which it is forced through a die to form a long tube containing either one or seven perforations. This tube is cut into the proper lengths to form the powder grains. The "green" powder from this operation still retains a considerable amount of ether and alcohol, most of which must be removed.

The green powder is dried to the desired final solvent content. Complete elimination of solvent is undesirable, because completely dry powder burns too fast for satisfactory use as a propellant, and also because completely dry powder is so hydroscopic that it changes rapidly in moisture content and in ballistic properties when exposed to air.

The solvent is recovered from the powder by either of two methods. In the older method the powder is placed in a

The lumps obtained are finally reduced to a powder by means of a "finishing" press, which consists of a pair of steel rollers or equivalent tools. The block is then placed in a "measuring press", from which it is forced through several small holes, so arranged as strings that "not like macaroni.

These strings are placed in a final "finishing press", which may be the same press used for preliminary finishing, and reformed into a cylinder. In this operation the pressure is maintained for one or two minutes; this application of pressure completes the solidifying.

The block from the final press is placed into the grinding press, from which it is forced through a die to form a long tube containing either one or seven perforations. This tube is cut into the proper lengths to form the powder grains. The "green" powder from this operation still retains a considerable amount of ether and alcohol, most of which must be removed.

The green powder is dried to the desired final solvent content. Complete elimination of solvent is undesirable, because completely dry powder burns too fast for satisfactory use as a propellant, and also because completely dry powder is so hygroscopic that it changes rapidly in moisture content and in ballistic properties when exposed to air.

The solvent is recovered from the powder by either of two methods. In the older method the powder is placed in a

closed system and air, at about 60° C., is circulated through it. The warm air removes most of the solvent from the powder, and the solvent is then removed from the air by cooling or by scrubbing with a suitable solvent. The process requires careful control, since the powder, on drying, tends to form a surface skin through which further passage of the solvent from the interior is very slow.

The newer method of solvent recovery is known as "water drying". In this process, warm water is used instead of air. The water causes the formation of microscopic cracks and pores on the surface of the powder, thus preventing the formation of the surface skin and allowing the solvent to pass from the interior of the grain into the water. The alcohol and ether pass into the water because they are more soluble in water than in powder. Thus the process is really one of extraction. In addition to more effective drying, this process reduces the warping customarily suffered by air-dried powder.

When the solvent has been sufficiently removed, the powder is taken out of the water, and the surface water is removed in a dryer. The finished powder contains about 3 per cent of volatile matter in the interior of the grain and about 1 per cent of surface water. Most of this is actually contained in the microscopic cracks and pores on the surface.

The amount of water held on the surface is extremely important in affecting the stability of the powder. The amount of water should be such that there is little tendency

closed system can air, at about 140° C., be circulated through it. The warm air recovers most of the solvent from the powder, and the solvent is then removed from the air by condensing or by scrubbing with a suitable solvent. The process permits certain control, since the powder, on drying, tends to form a surface skin through which further passage of the solvent from the interior is very slow.

The novel method of solvent recovery is known as "water drying". In this process, warm water is used instead of air. The water causes the formation of microscopic cracks and pores on the surface of the powder, thus preventing the formation of the surface skin and allowing the solvent to pass from the interior of the grain into the water. The alcohol and other pass into the water because they are more soluble in water than in powder. Thus the process is really one of extraction. In addition to more effective drying, this process reduces the marring customarily suffered by air-dried powder.

When the solvent has been sufficiently removed, the powder is taken out of the water, and the surface water is removed in a dryer. The finished powder contains about 3 per cent of volatile matter in the interior of the grain and about 1 per cent of surface water. Most of this is actually contained in the microscopic cracks and pores on the surface.

The amount of water held on the surface is extremely important in affecting the stability of the powder. The amount of water should be such that there is little tendency

for the moisture to evaporate in dry weather or for the powder to take up water during humid weather.

After drying, the powder from several batches is blended to produce a large quantity of essentially uniform powder. Such a quantity is called a "lot". The powder from each lot is generally kept together and assigned to be used by the same ship or battery.

After blending, the powder is stored in metal-lined boxes sealed with rubber gaskets. Every effort is made to keep the containers watertight, to avoid the effects of changing humidity.

Stability of Smokeless Powder

Even pure nitrocellulose, in either the colloided or uncolloided state, tends to decompose slowly on standing, with the formation of nitric oxide and nitrogen dioxide. The rate of decomposition rises with the temperature; the reaction is accelerated by high humidity. In the presence of acid the rate of decomposition is very greatly increased. Nitrocellulose that has not been freed completely from sulfate esters of cellulose is much less stable than the thoroughly purified material. The sulfate esters hydrolyse more rapidly than the cellulose nitrate itself, and the traces of sulfuric acid set free by the hydrolysis catalyse the decomposition. The nitrate esters of hydrocellulose and oxycellulose also tend to make the powder unstable; they decompose readily to form oxides of nitrogen that can react with

for the nation, to evaporate in any weather or for the powder to have a very coarse granular condition.

After mixing, the water from several batches is blended to produce a large quantity of uniformly mixed cotton, such a quantity is called a "lot". The powder from each lot is generally kept together and designed to be used by one army or battery.

After blending, the powder is stored in metal-lined boxes sealed with rubber gaskets. Every effort is made to keep the contents "sweet", to avoid the effects of storage-ing humidity.

<u>Stability of Smokeless Powder</u>

Even pure nitrocellulose, in either the colloided or uncolloided state, tends to decompose slowly on standing, with the formation of nitric oxide and nitrogen dioxide. The rate of decomposition rises with the temperature; the reaction is accelerated by high humidity. In the presence of acid the rate of decomposition is very greatly increased. Nitrocellulose that has not been freed completely from sulfate esters of cellulose is much less stable than the thoroughly purified material. The sulfate esters hydrolyze more rapidly than the cellulose nitrate itself, and the traces of sulfuric acid set free by the hydrolysis catalyze the decomposition. The nitric esters of nitrocellulose and cellulose also tend to make the powder unstable; they decompose readily to form oxides of nitrogen that can react with

any moisture present to form acids that catalyse the decomposition of the true nitrocellulose.

Although well purified nitrocellulose is rather stable and does not begin to break down readily at room temperature, a small amount of decomposition does take place within a relatively short period of time. The oxides of nitrogen produced by this decomposition attack the nitrocellulose very rapidly, causing further decomposition. Thus, if these oxides are not removed, the decomposition is "auto-catalytic" and its rate increases rapidly, causing considerable decomposition in a short time. For this reason there must be added to the smokeless powder some compound which will react with the oxides as fast as they are formed, tying them up as some compound which does not further the decomposition. Such an additional compound is called a stabilizer, and powder to which it has been added is said to be stabilized.

Stabilizers

There are two important requirements for a good stabilizer in addition to the obvious one that it must react with the oxides of nitrogen formed by the decomposition of nitrocellulose.

First, neither it nor the product of its reaction with the oxides of nitrogen should react with the nitrocellulose. Thus the use of an alkali as a stabilizer is not feasible, because both the alkali and the nitrates and nitrites formed from it react very rapidly with nitrocellulose. (1)

any nitrogen present to form acids that catalyze the decomposition of the nitrocellulose.

Although well purified nitrocellulose is rather stable and does not begin to break down readily at room temperature, a small amount of decomposition does take place within a relatively short period of time. The oxides of nitrogen produced by this decomposition attack the nitrous ester very rapidly, causing further decomposition. Thus, if these oxides are not removed, the concentration is "auto-catalytic" and the rate increases rapidly, causing considerable decomposition in a short time. For this reason there must be added to the smokeless powder some compound which will react with the oxides as fast as they are formed, being thus up as more compound which does not further the decomposition. Such an additional compound is called a stabilizer, and powder to which it has been added is said to be stabilized.

Stabilizers

There are two important requirements for a good stabilizer in addition to the obvious one that it must react with the oxides of nitrogen formed by the decomposition of nitrocellulose.

First, neither it nor the product of its reaction with the oxides of nitrogen should react with the nitrocellulose. Thus the use of an alkali as a stabilizer is not feasible, because both the alkali and the nitrites and nitrites formed from it react very rapidly with nitrocellulose. (1)

Second, neither the stabilizer nor its products should destroy the homogeneity of the powder. Calcium carbonate, which is a good stabilizer for dynamite, cannot be used for smokeless powder because it is insoluble and remains as a finely divided solid in the powder. Urea, which otherwise is a very good stabilizer, cannot be used because it produces bubbles of nitrogen gas in the powder.

The stabilizer should also be relatively cheap, and both it and its products must be themselves stable.

Stabilizers have been used in smokeless powder ever since its first manufacture in France in 1884. The first substance used was amyl alcohol (2), which reacts with the oxides of nitrogen to form esters, amyl nitrite and amyl nitrate. These esters are in turn attacked by the oxides, and break down, releasing nitric and nitrous oxides, and at the same time the amyl radical is oxidised to valeric acid. The presence of valeric acid can readily be detected by its odor, and its presence was taken as evidence that the amyl alcohol was exhausted and the powder no longer stable. Since each molecule of amyl alcohol reacts with only one nitrogen, which it later gives up, amyl alcohol is a very poor stabilizer. Its use was abandoned, but not until two French warships had been destroyed by explosions attributed to spontaneous inflammation of the powder in their magazines. The Italians used aniline as a stabilizer, but since aniline itself attacks nitrocellulose, it makes a very poor stabilizer and its use was soon discontinued.

[illegible] and [illegible] stabilizer and [illegible] [illegible]

[illegible] the composition of the powder, [illegible] [illegible], which is a [illegible] [illegible] [illegible], [illegible] [illegible] used for smokeless [illegible] [illegible] [illegible] [illegible] and reacting as a highly divided [illegible] in the powder. [illegible], [illegible] [illegible] [illegible] [illegible] good stabilizer, [illegible] be used [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible].

The stabilizer should also be relatively cheap, and both it and its products must be innocuous stable.

Stabilizers have been used in smokeless powder ever since the first smokeless in France in 1886. The first substance used was amyl alcohol (5), which reacts with the oxides of nitrogen as fast as they [illegible] and amyl nitrite.

These esters are in turn attacked by the oxides, and break down, releasing nitric and nitrous oxides, and at the same time the amyl nitrite is oxidized to valeric acid. The presence of valeric acid can readily be detected by its odor, and its presence was taken as evidence that the amyl alcohol was exhausted and the powder no longer stable. Since each molecule of amyl alcohol reacts with only one nitrogen, which it later gives up, amyl alcohol is a very poor stabilizer. Its use was abandoned, but not until the French warship has been destroyed by explosions attributed to spontaneous inflammation of the powder in their magazines. The Italians used aniline as a stabilizer, but since aniline itself attacks nitro-cellulose, it makes a very poor stabilizer and its use was soon discontinued.

By far the most important stabilizer is diphenylamine, which was used as early 1909 and is still the standard in most countries, including the United States.

The only substance which can compete with diphenylamine as a stabilizer is "Centralite", a trade name for any of several alkyl-substituted diphenyl ureas, the most usual being symmetrical diethyl diphenyl urea. However the centralites are used chiefly as solvents and coatings. In this paper diphenylamine and centralite will be discussed in detail, followed by a list of other compounds which have been used or proposed and a discussion of the comparative stabilization powers of the various compounds.

Diphenylamine

Diphenylamine is by far the most important stabilizer for smokeless powder, although it is generally considered that centralite is actually a better stabilizer.

The qualities of diphenylamine as a stabilizer were first established by M. Marqueyrol in a series of researches lasting fifteen years (3). Samples of smokeless powder containing up to 10 per cent of diphenylamine were heated at five different temperatures for periods up to 4083 days, and samples were removed from time to time for analysis of the nitrogen content of the nitrocellulose. Up to that time it was generally considered that smokeless powder decomposed at a rapid and uncontrollable rate. Marqueyrol's tests established the fact that nitrocellulose is essentially stable and loses stability only

by far the most important stabilizer in diphenylamine, which are used as early 1[illegible] and is still the standard in most countries, including the United States.

The only substance which can compete with diphenylamine as a stabilizer is "Centralite", a trade name for any of several alkyl-substituted diphenyl ureas, the most usual being symmetrical diethyl diphenyl urea. However the centralites are used chiefly as solvents and coatings. In this paper diphenylamine and centralite will be discussed in detail, followed by a list of other compounds which have been used or proposed and a discussion of the comparative stabilization powers of the various compounds.

<u>Diphenylamine</u>

Diphenylamine is by far the most important stabilizer for smokeless powder, although it is generally considered that centralite is actually a better stabilizer.

The qualities of diphenylamine as a stabilizer were first established by K. Marqueyrol in a series of researches lasting fifteen years (3). Samples of smokeless powder containing up to 10 per cent of diphenylamine were heated at five different temperatures for periods up to 4083 days, and samples were removed from time to time for analysis of the nitrogen content of the nitrocellulose. Up to that time it was generally considered that smokeless powder decomposed at a rapid and uncontrollable rate. Marqueyrol's tests established the fact that nitrocellulose is essentially stable and loses stability only

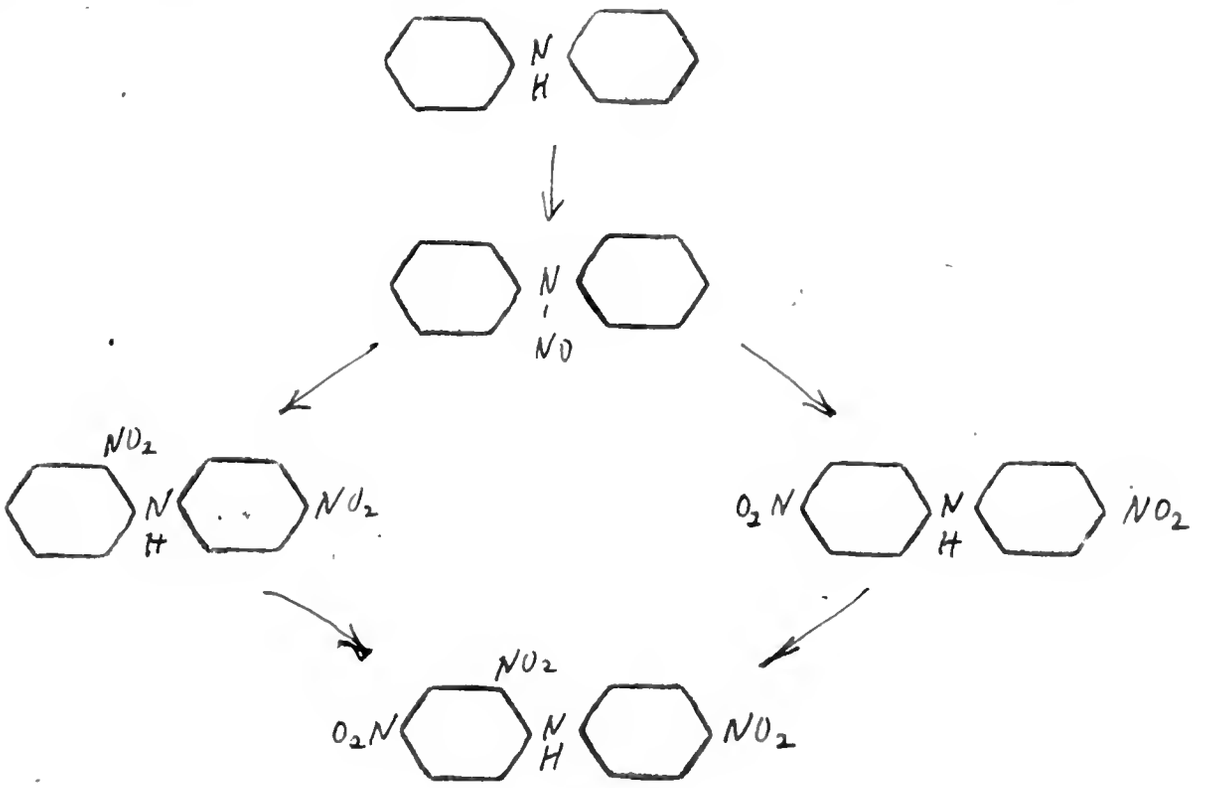
when in contact with slight amounts of its decomposition products. He showed that the first reaction product of diphenylamine is diphenylnitrosamine, which is itself a better stabilizer than diphenylamine. This is due to the fact that nitrosamine is a gelatinizer for nitrocellulose, and remains intimately mixed with it, whereas diphenylamine does not. However at elevated temperatures the nitrosamine has very poor stabilizing power.

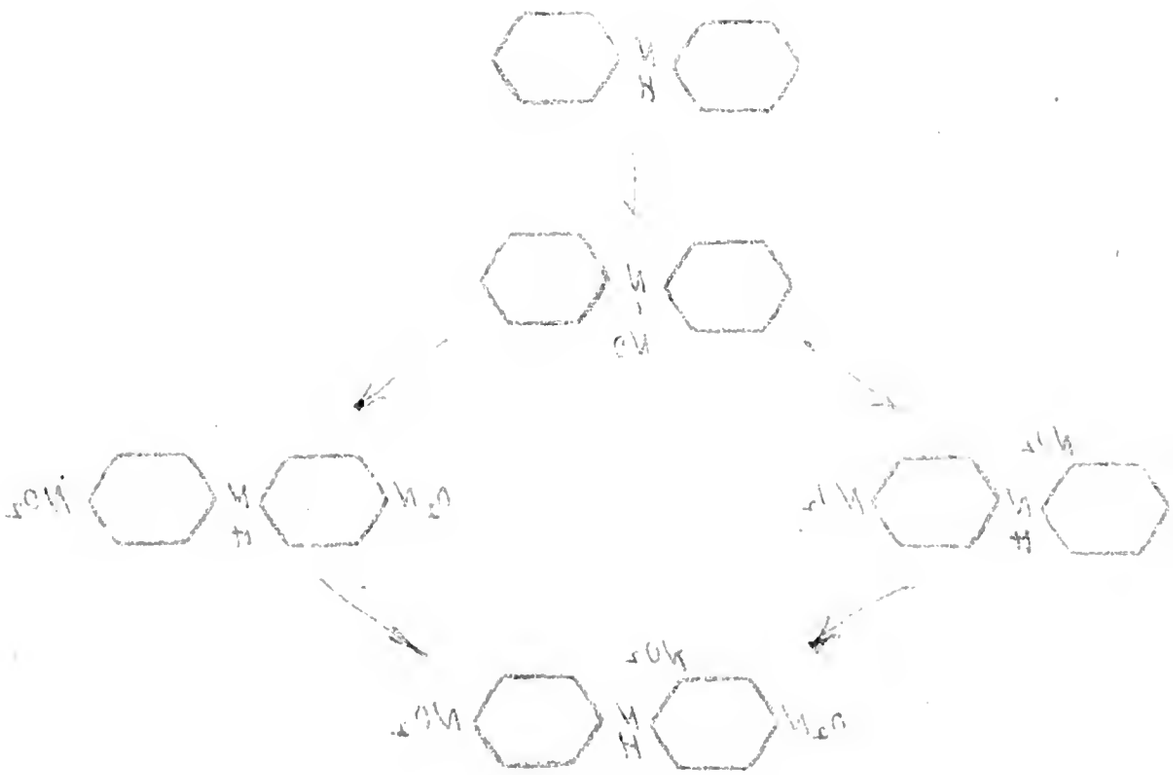
These tests also showed that the effect of temperature is very important on the action of a stabilizer, since some of the reaction products may themselves be unstable at certain temperatures. Therefore any test for stabilization should be run at at least two temperatures. These observations in regard to the effect of temperature were confirmed by other researchers (4) (5) who also found that the presence or absence of oxygen and the amount of moisture present in the powder also materially affected the results.

Marqueyrol and others have studied the derivatives of diphenylamine which cause powder to darken with age, and have concluded that they are due to impurities in the ether used in the powder or to the oxidising action of the air during drying, and are not products of a reaction between diphenylamine and nitrocellulose or the oxides of nitrogen. (6) (7) (8). The principal oxidation product producing darkening is diphenyl dihydro phenazine.

The transformations undergone by diphenylamine as a result of the decomposition of the powder have been studied

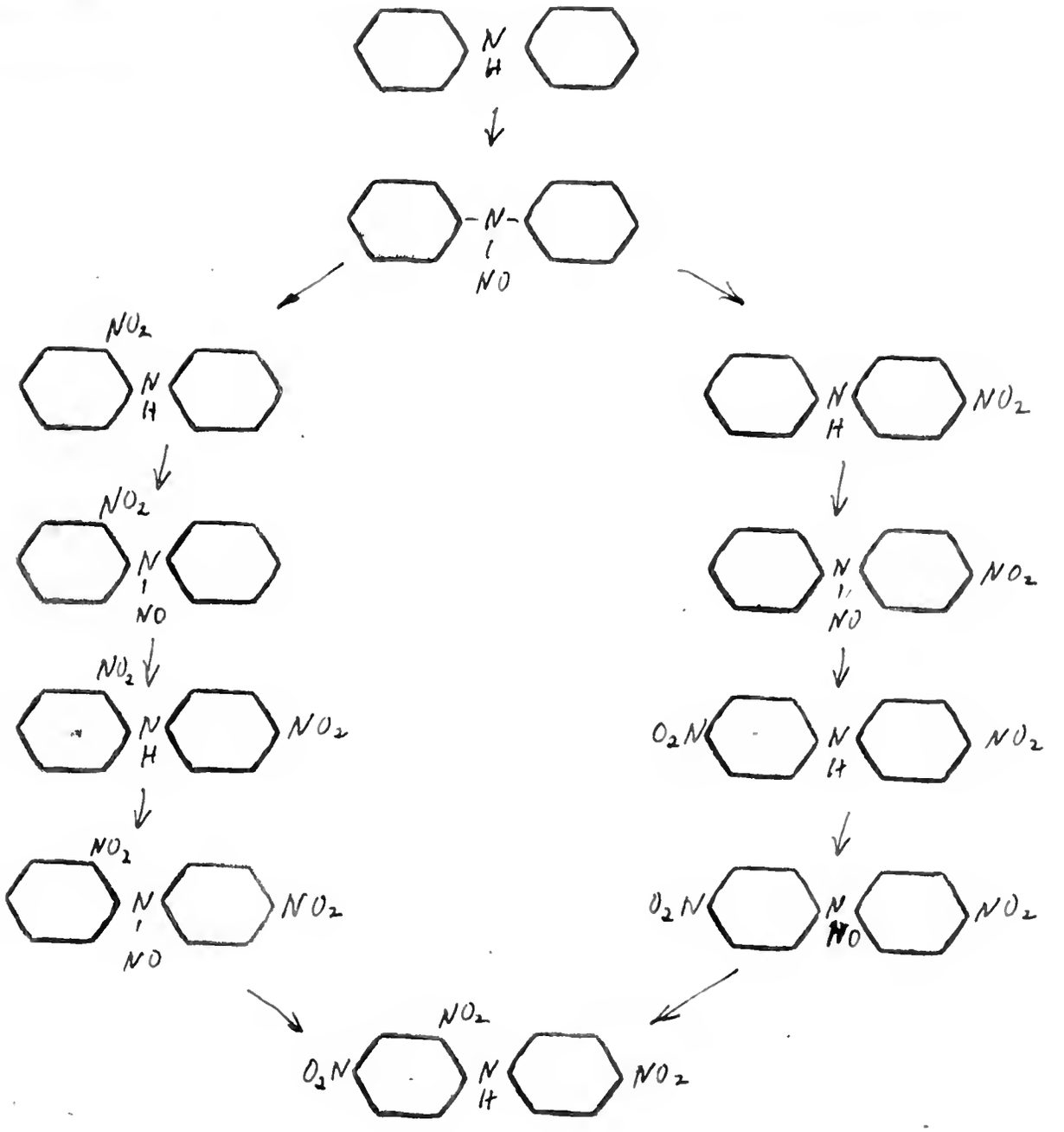
by several investigators and seem to be fairly well established. The chief work in this field was done by Davis and Ashdown at M. I. T., working under a contract for the U. S. Army. (9) (10) They prepared all the compounds which might be expected to be formed by nitration of diphenylamine and devised color tests to indicate the presence of each of them, as well as methods of separating each from mixtures of one another and nitrocellulose. These separations and tests were applied to diphenylamine-stabilized powders in various stages of decomposition, the most advanced being a powder that had been giving off fumes for several months. These tests indicate that the reactions are as follows:

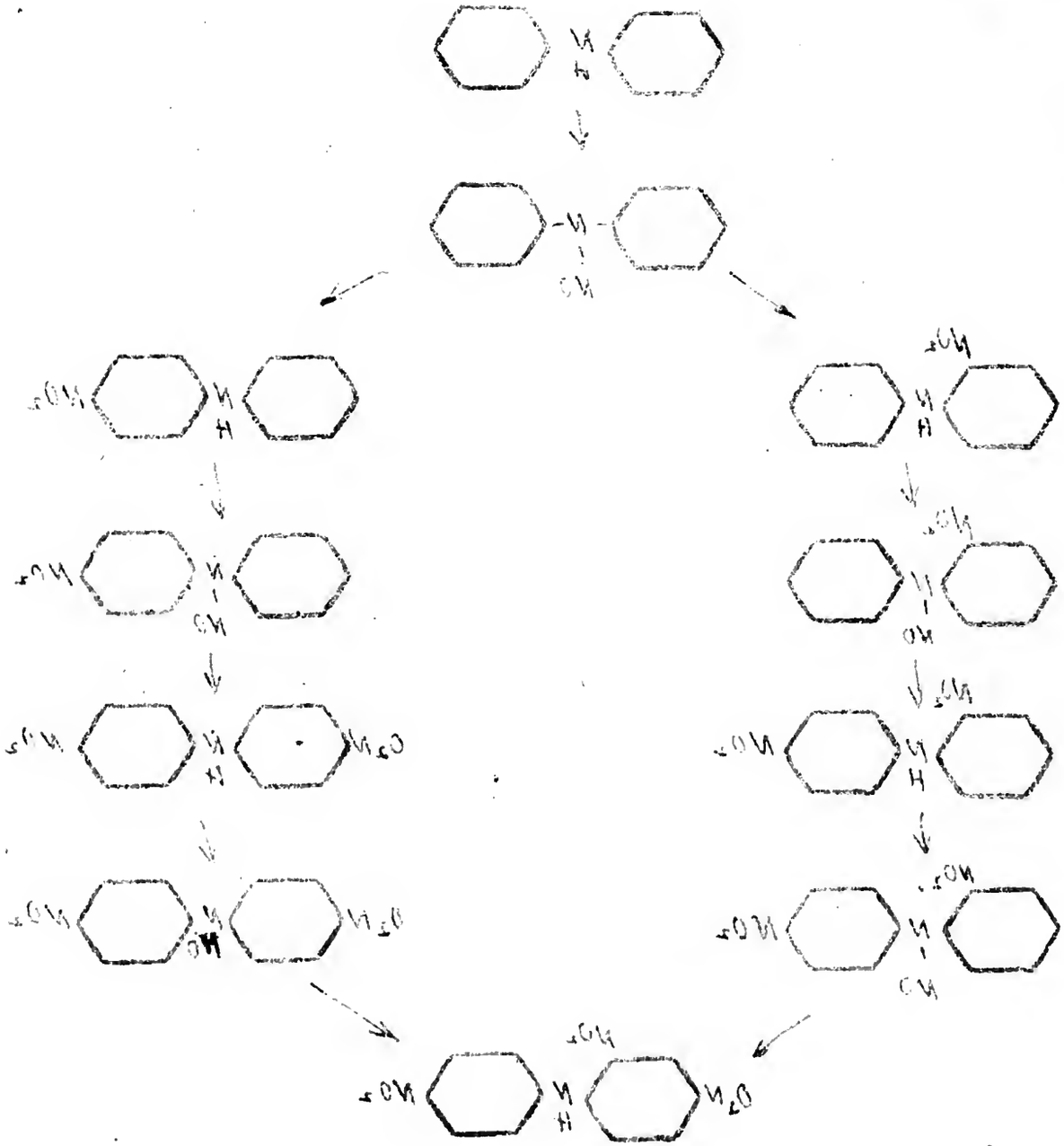




The last product formed, 2-4-4' trinitrodiphenylamine, might be expected to undergo further nitration to the 2-4-2'-4' tetranitro compound, but rather exhaustive attempts to isolate this compound were not successful.

Becker and Hunold, (11), confirm the fact that the tetranitro product is not formed. They also isolated several more intermediate compounds. Their proposed reactions are as follows:





The two mechanisms lead to the same end product, a trinitro derivative. The fact that diphenylamine takes up three nitro groups per molecule is one of the reasons that the compound is such a good stabilizer.

Becker and Hunold also measured the relative time required for the formation of the various compounds from powder containing diphenylamine, which was kept at 100° C. The nitrosamine was detected even before heating, the mononitro compound after one day at the elevated temperature, the dinitro after two days and the trinitro after four days.

They also tested the stabilizing power of the various intermediates by preparing powders containing each of these compounds. The relative values were as might be expected, except that the last product, the trinitro compound, was a better stabilizer than the compounds immediately preceding it, the dinitro diphenylnitrosamines. Since neither of these actually takes up any more nitrogen, it is hard to see how either can act as a stabilizer. No explanation was offered.

There is some evidence that the reaction is not as simple as the above discussion might indicate. The effect of temperature has been largely ignored in both the above experiments, but other workers have found that the reaction is apparently different at different temperatures. It was found (12) that stabilized powders decomposed at a rate which was only one-fifth to one-sixth that of unstabilized powder at 50° C., but at 77.5° C. its reaction rate was one-third that of the unstabilized powder.

[illegible] to the [illegible] and pressure, a [illegible] derivative. [illegible] chlorophyllide taken up [illegible] groups per molecule [illegible] of the reasons why [illegible] compound is such a good [illegible].

[illegible] measured the relative time required for the formation of [illegible] compounds from pheophorbide containing chlorophyllide, when [illegible] at 100° C. The chlorophyllides were detected over [illegible] in time, the reversion compound after one day at the elevated temperature. The difference after two days and the difference after four days.

They also tested the stabilizing power of the various [illegible] by preparing reactions containing each of these compounds. The relative values were as might be expected, except that the last product, the [illegible] compound, was a better stabilizer than the compounds immediately preceding it, the chlorophyllin chlorophyllin-compounds. Since neither of these actually takes up any more nitrogen, it is hard to see how either can act as a stabilizer. No explanation was offered.

There is some evidence that the reaction is not as simple as the above discussion might indicate. The effect of temperature has been largely ignored in both the above experiments, but other workers have found that the reaction is apparently different at different temperatures. It was found (12) that stabilized powders decomposed at a rate which was only one-fifth to one-sixth that of unstabilized powder at 50° C., but at 77.5° C. the reaction rate was one-third that of the unstabilized powder.

This would indicate either that the reactions are different at different temperatures, or that the method of testing is inaccurate. The low-temperature test may not indicate the true velocity of decomposition.

It was also found (13) that a catalyst was necessary to carry out the reaction between diphenylamine and oxides of nitrogen in the laboratory. Chlorides and copper salts were used as catalysts. It is supposed that the small amounts of copper salts present in smokeless powder from the various manufacturing containers act as catalyst when the reaction occurs in powder.

It has also been observed that the purity of the diphenylamine and of the nitrocellulose affect the stability. (14) Powders made in 1912 with normally stabilized nitrocellulose and purified diphenylamine showed no loss of stability when tested after twenty years storage at room temperature, while powder manufactured during the first World War, using rapidly stabilized nitrocellulose and technical diphenylamine, showed marked losses of stability in fifteen years.

In this connection it is interesting to note that it is possible to restabilize powder with diphenylamine. The process (15) is performed by softening the powder in alcohol, without altering the grain size, and then re-impregnating with diphenylamine in alcohol solution.

Powder which has been stabilized with diphenylamine may be tested for stability and suitability for further use rather easily. A powder is considered unfit for further

[illegible] different at different temperatures, [illegible] a treating the powders are. [illegible] the rate of decomposition.

It was also [illegible] that [illegible] was necessary to carry out the [illegible] nitrogen and oxygen [illegible] in the laboratory. [illegible] and oxygen [illegible] as catalysts. [illegible] amounts of [illegible] water [illegible] water [illegible] combination [illegible] when the [illegible] in powder.

It has also been observed that the purity of the diphenylamine and of the nitrocellulose affect the stability.

(14) Powders made in 1932 with recently established nitrocellulose and purified diphenylamine showed no loss of stability when tested after twelve years storage at room temperature, while powder manufactured during the first World War, using rapidly established nitrocellulose and technical diphenylamine, showed marked losses of stability in fifteen years.

In this connection it is interesting to note that it is possible to neutralize powder with diphenylamine. This process (15) is performed by soaking the powder in alcohol, without altering the grain size, and then re-impregnating with diphenylamine in alcohol solution.

Powder which has been established with diphenylamine may be tested for stability and suitability for further use rather easily. A powder is considered unfit for further

storage if all of the diphenylamine and the diphenylnitrosamine have been exhausted. These compounds may be detected in an alcohol extract of the powder by simple color tests as follows:

If diphenylamine is present, a strip of filter paper on which an alcoholic extract of the powder has been allowed to dry is colored blue by a drop of ammonium persulfate. Also, if the extract contains diphenylamine it is colored blue by the addition of a few drops of a saturated solution of ammonium persulfate. Diphenylnitrosamine gives no color with ammonium persulfate, but imparts an intense blue color to a few milliliters of cold concentrated sulfuric acid.

Centralite

The first centralite was symmetrical dimethyl diphenyl urea. It was called centralite because it was developed at the Central War Laboratory in Germany. The ethyl compound, symmetrical diethyl diphenyl urea, usually called Centralite No. 1, is now more common; the methyl compound is now called Centralite No. 2.

The reaction of centralite with oxides of nitrogen has also been studied rather intensively, but opinion as to the nature of the reaction differs. One belief is that the reaction is simple nitration, forming first a dinitro compound with nitro groups substituted in the para positions of the two phenyl rings, and finally a tetranitro compound with two ortho and two para positions substituted (16). Another theory is that the centralite molecule is broken up, forming p-nitro phenyl ethyl

storage [illegible] the dihydro [illegible] [illegible] have been considered. [illegible] is defined in an [illegible] sense of the [illegible] [illegible] follows:

[illegible] [illegible] [illegible] [illegible] [illegible] power or [illegible] [illegible] [illegible] [illegible] [illegible] allowed [illegible] [illegible] [illegible] [illegible] [illegible]

nitrosamine. (17) In either case, it should be noted that one centralite molecule takes up four nitro groups, which is one more than diphenylamine can absorb.

Other Compounds

Many other compounds have been used, or at least proposed, as stabilizers. Not much is known about the reactions they undergo, but a great many comparisons have been made as to the relative powers of stabilization. Some of the more important suggested substances are:

acardite (assymmetrical diphenyl urea)
alpha naphthyl urethane
camphor
carbazole
diamyl phthalate
diphenylbenzamide
ethyl oxinilate
mucic acid
naphthalene
nitro naphthalene
phenanthrene
potassium oxinilate
petrolatums of various kinds
phthalide
substituted urethanes
saccharic acid
tartaric acid

[illegible]

[illegible]

[illegible]

triacetate of methyl trimethylol methane (18)

triphenylamine

Comparison of Stabilizing Power

Many workers have made comparisons of the stabilizing power of various groups of the compounds listed above. However it is rather difficult to integrate the results, since methods differed widely and since each worker compared only a few compounds. The results of some of the more important experiments are given below:

Marqueyrol, in his work mentioned above, also made comparisons of the stabilizing power of several compounds. These included amyl alcohol, diphenylamine, nitronaphthalene, naphthalene, diphenyl benzamide, diphenyl nitrosamine, and carbazole. He, of course, concluded that diphenylamine was the best stabilizer, and it was his work that first promoted the use of this compound. However, he found that for some temperatures the benzamide was better, and he also found that carbazole, while not as good a stabilizer as diphenylamine, has less direct action on the nitrocellulose at high temperatures, and therefore can be used in larger quantities with safety.

Giua and Guastalla (19) ran comparative tests on several compounds. They concluded that the compounds under consideration could be arranged in order of decreasing stabilizing effect as follows:

Diphenylamine

Centralite

Carbowax 20 M, Methyl Methacrylate Methane (16)

Triphenylamine

Comparison of Stabilizing Power

Many workers have made comparisons of the stabilizing power of the compounds listed above. However, it is rather difficult to integrate the results, since methods differed widely and some each worker compared only a few compounds. The results of some of the more important experiments are given below:

Bergquist, in the work mentioned above, also made comparisons of the stabilizing power of several compounds. These included ethyl alcohol, diphenylamine, nitrosophenolamine, naphthalene, triphenyl benzenes, diphenyl nitrosamine, and carbazole. He, of course, concluded that diphenylamine was the best stabilizer, and it was his work that first promoted the use of this compound. However, he found that for some temperatures the benzenes was better, and he also found that carbazole, while not as good a stabilizer as diphenylamine, has less direct action on the nitrocellulose at high temperatures, and therefore can be used in larger quantities with safety.

Otis and Guastalla (15) ran comparative tests on several compounds. They concluded that the compounds under consideration could be arranged in order of decreasing stabilizing effect as follows:

Diphenylamine

Centralite

Aniline

alpha Naphthylurethane

Ethyl Oxinilate

Potassium Oxinilate

Phthalide

M. Tonegutti, (20) (21), found that diphenylamine and centralite were of equal power and were the best stabilizers of all he tested. Disubstituted urethanes were good stabilizers when mixed with acardite, but not alone, while phthalide and diamyl- and dibutyl-phthalates had no stabilizing action at all. Substances that are both stabilizers and gelatinizers gave very good results when mixed with substances which are stabilizers only, producing better stabilization than either substance used alone. Phenanthrene gave very good results on nitroglycerine powders. He concluded that diphenylamine is the best stabilizer for double-base powders, but acardite is the best for single-base powders.

Tonegutti also compared the stabilizing power of various petrolatums, since these were being seriously considered at that time. (22) As might be expected, it was found that those having the highest degree of unsaturation (as shown by the bromine number) were the best stabilizers.

R. Dalbert (23) compared powders containing 8.75 per cent of centralite with powders in which 2 per cent of the centralite had been replaced with either diphenylamine or carbazole. In each case, the straight centralite was the best,

[illegible]

diphenylamine

straight dynamite

Cohesive dynamite

Dynoxide

2. Tonegutti, (4) (23), found that diphenylamine was actually only of equal power and was the best stabilizer of all he tested. Diphenylamine mixtures were good stabilizers when mixed with centralite, but not alone, while phenylalpha and diphenyl-phenylalpha had no stabilizing action at all. Substances that are both stabilizers and gelatinizers gave very good results when mixed with substances which are stabilizers only, producing better stabilization than either substance used alone. Phenomenons gave very good results as nitroglycerine powders. He concluded that diphenylamine is the best stabilizer for double-base powders, but centralite is the best for single-base powders.

Tonegutti also compared the stabilizing power of various petrolatums, since these were being extensively considered at that time. (23) As might be expected, it was found that those having the highest degree of saturation (as shown by the Bromine number) were the best stabilizers.

3. Dubbert (25) compared powders containing 8.75 per cent of centralite with powders in which 2 per cent of the centralite had been replaced with either diphenylamine or carbocole. In each case, the straight centralite was the best,

the carbazole being the worst.

Dalbert also studied the action of triphenylamine as a stabilizer, comparing its action to that of diphenylamine. (24) Powders containing two and five per cent of triphenylamine were compared with similar powders containing diphenylamine. The two-per cent powders showed similar action when heated to 100° C. but powder containing five per cent of triphenylamine showed less denitration than the corresponding diphenylamine powder. No nitroso compound was formed from the triphenylamine, the first product being a mononitro compound. These tests seem to indicate that triphenylamine might make a superior stabilizer, but apparently no further work has been done towards confirming this.

Krauz and Majrach considered the action of di- and tri- carboxylic acids, using tartaric acid as typical. Tartaric acid took up two nitro groups, forming dinitro tartaric acid. This compound when heated in aqueous solution decomposed into carbon dioxide, nitrogen trioxide, nitrogen, and a small amount of carbonic acid. If heated dry, the gases varied with temperature, glyoxalic acid being left in the solid residue. (25)

The same two workers also studied the nitro esters of other dicarboxylic acids, namely glutaric, mucic, and saccharic. These were found to act very much like tartaric acid, and to be better stabilizers than tartaric acid. (26)

Desmaroux (27) studied the comparative stabilizing effects of camphor and centralite, and concluded that camphor was

the carbonate being [illegible].

Hallwes also studied the action of trihydroxybenzoic as a catalyst, comparing [illegible] of triphenylmethane. (24) Tertiary carbinols [illegible] per cent of triphenylmethane were compared with [illegible] catalysts [illegible] triphenylmethane. The two-per cent product, dried [illegible] when heated to 100° C. the product contained five per cent of triphenylmethane showed less decomposition than the corresponding diphenylmethane product. No [illegible] was formed from the triphenylmethane, the first product could [illegible] or ground. These tests seem to indicate that triphenylmethane might make a superior catalyst, but apparently no further work has been done towards confirming this.

Evans and Taylor considered the action of dia- and tri- carboxylic acids, using tartaric acid as typical. Tartaric acid took up two atoms groups, forming fixed tartaric acid. The compound when heated in aqueous solution decomposed into carbon dioxide, nitrogen tetroxide, nitrogen, and a small amount of carbonic acid. If heated dry, the gases varied with temperature, glycolic acid being left in the solid residue. (25)

The same two workers also studied the nitro esters of other dicarboxylic acids, namely glutaric, succic, and succinic. These were found to act very much like tartaric acid, and to be better stabilizers than tartaric acid. (26)

Desmarous (27) studied the comparative stabilizing effects of camphor and centralite, and concluded that camphor was

as good as centralite, at least for periods up to 600 days, which was the longest test conducted.

Testing for Stability of Powder

No really satisfactory method of testing the stability of smokeless powder has as yet been devised. For research problems, such as comparing the stabilizing effect of various substances, the reduction in nitrogen content is taken as a measure of instability. Thus to compare two stabilizers, powders containing each are prepared, and rather large samples of each kept under carefully controlled conditions of temperature and humidity for a long time. From time to time, samples of each are withdrawn and analysed for nitrogen, the powder which has lost the least being considered the better stabilized. This method presents several difficulties and is really not very satisfactory. The nitrocellulose must be removed from the stabilizer and its products and tested for its nitrogen content. This presents difficulties and the method employed varies with the type of powder and the stabilizer. In addition, as has been mentioned before, the temperature plays an important part in the effective stability, some substances acting as very good stabilizers at one temperature but being very poor at other temperatures either higher or lower. Accordingly, such tests should be run at several temperatures.

Several methods have been used for testing stability without waiting for the actual decomposition to occur, as in the above tests. These are usually referred to as

[illegible]

[illegible]

[illegible]

[illegible]

stability of emulsions; [illegible] mean devices. For measure [illegible], such as [illegible] taking effect on natural oils [illegible] a [illegible] to [illegible] a measure of [illegible] ity. Then to measure the stabilizers, positive [illegible] used as [illegible], are taken large samples in each kept under controlled [illegible] conditions of temperature and humidity for a long time. From time to time, samples of each are examined and analyzed for [illegible], the powder which has lost the lemon being considered the better stabilizer. This method presents several difficulties and is really not very satisfactory. The antioxidants must be removed from the stabilizer and the products and tested for its nitrogen content. This presents difficulties and the method employed varies with the type of powder and the stabilizer. In addition, as has been mentioned before, the temperatures plays an important part in the effective stability, some substances acting as very good stabilizers at one temperature but being very poor at other temperatures either higher or lower. Accordingly, such tests should be run at several temperatures.

Several methods have been used for testing stability without waiting for the natural decomposition to occur, as in the above tests. These are usually referred to as

"heat tests". The two most common of these in this country are the 65.5° C. KI starch test and the 134.5° C. methyl violet test.

In the KI starch test, the powder samples are heated in test tubes at 65.5° C. Within each tube, a strip of KI starch paper, spotted with a 50 per cent aqueous solution of glycerine, is hung from a platinum hook. The tubes are stoppered with cork. The tubes are examined constantly and the time required for the first appearance of color on the paper is reported. Specifications in the United States call for at least 35 minutes before the first appearance of color.

In the methyl violet test, long tubes of heavy glass are used. They are closed loosely with notched corks, and are heated for almost their whole length in a bath at 134.5° C. The sample occupies about two inches of the lower end of the tube, and strips of methyl violet paper are placed about one inch above the sample. Times are noted for the paper to be turned completely to a salmon-pink color, for the first appearance of red fumes, and for explosion. Explosion usually does not occur for about five hours.

It will be noted that neither of the above gives a true indication of stability, since they measure the time for the self-catalyzed reaction in an atmosphere of air or red fumes. They thus serve only to compare the stability of powders which are similar in other respects. For true observations of stability, a heat test under vacuum is necessary.

"Heat Bands", the two most [illegible] of these in this country are the [illegible] at Ottawa and [illegible] at [illegible], methyl violet band.

In the [illegible] band, the reader samples are located [illegible]. Within each tube, a strip of [illegible] paper, coated with a 50 per cent aqueous solution of glycerine [illegible] from a [illegible] hook. The tubes are stoppered [illegible]. The tubes are mounted vertically and the [illegible] for the film's appearance of color on the paper is reported. Accelerated [illegible] in the United States call for at least 50 [illegible] before the first appearance of color.

In the methyl violet band, long tubes of heavy glass are used. They are closed loosely with notched corks, and are [illegible] over almost their whole length in a bath at 124.4° F. The sample consists about two inches of the lower end of the [illegible], and strips of methyl violet paper are placed about one inch above the sample. These are noted for the paper to be turned completely to a salmon-pink color, for the first appearance of red tones, and for exploded. Explosion usually does not occur for about five hours.

It will be noted that neither of the above gives a true indication of stability, since they measure the time for the self-catalyzed reaction in an atmosphere of air or red fumes. They thus serve only to compare the stability of powders which are similar in other respects. For true observations of stability, a heat test under vacuum is necessary.

Effects of Temperature and Humidity on Stability

If smokeless powder is exposed to a humid atmosphere, it will absorb moisture slowly. Conversely, it will give up moisture to a dry atmosphere. The extent of both of these is dependent on the amount of surface moisture present originally in the powder, as mentioned above. The hygroscopicity also seems to depend on the total amount of nitrocellulose present, so that double base powders are less hygroscopic than straight nitrocellulose powder.

The amount of moisture present has a very marked effect on the stability. In one experiment a powder was exposed to a saturated atmosphere for three months at 50° C. After this exposure, it was kept at 65.5° C. in a closed container, red fumes appearing after nine days. The same powder, unexposed to the humid atmosphere, took 540 days to produce red fumes under the same conditions. (28)

Changes in temperature and humidity affect the stability of powder in another fashion, also. As the powder takes up moisture, the water and volatile matter in the powder move inward from the surface toward the interior. If the same powder then loses water, due to a change in conditions, this water moves outward. Thus there is a constant shifting of the liquid within the powder. This tends to break up the structure of the grain and promote decomposition.

Smokeless powder deteriorates much more rapidly at high than at low temperatures. This is due partly to the

Effects of Temperature and Humidity on Stability

If smokeless powder is exposed to a humid atmosphere, it will absorb moisture readily. Correspondingly, it will give up moisture to a dry atmosphere. The extent of both of these is dependent on the amount of moisture present initially in the powder, as mentioned above. The hygroscopicity also seems to depend on the total amount of nitrocellulose present, so that double base powders are less hygroscopic than straight nitrocellulose powder.

The amount of moisture present has a very marked effect on the stability. In one experiment a powder was exposed to a saturated atmosphere for three months at 100° C. After this exposure, it was kept at 65.5° C. in a closed container, and fumes appeared after nine days. The same powder, unexposed to the humid atmosphere, took 240 days to produce red fumes under the same conditions. (9)

Changes in temperature and humidity affect the stability of powder in another fashion, also. As the powder takes up moisture, the water and volatile matter in the powder move inward from the surface toward the interior. If the same powder then loses water, due to a change in conditions, this water moves outward. Thus there is a constant shifting of the liquid within the powder. This tends to break up the structure of the grain and promotes decomposition.

Smokeless powder deteriorates much more rapidly at high than at low temperatures. This is due partly to the

acceleration of the decomposition reaction of nitrocellulose and partly to the fact that the stabilizer also decomposes at high temperatures. Diphenylnitrosamine decomposes very easily as the temperature is raised, and hence the stability of diphenylamine powders decreases rapidly.

List of References

1. Taylor and Baker, Sidgwick's Organic Chemistry of Nitrogen, Oxford Press.

2. Davis, The Chemistry of Powder and Explosives, John Wiley and Sons.

3. M. Marqueyrol, Study of Different Stabilizers, Mem. Poudres 23, 178-82 (1928) C. A. 23, 5043.

4. J. Mecir and F. Sillinger, Chemical Stabilization of Smokeless Powders, Compt Rendu. 17me Congr. Chim. Ind., Paris Sept.-Oct. 1937, pp. 832-9, C. A. 32, 6867.

5. Apard, Stability of Nitroglycerine Powders, Mem. Poudres 27, 11-47 (1937),C. A. 31, 7648.

6. Desmaroux, Origin of Colored Spots in Powder B, Mem. Poudres, 21, 238-258 (1924), C. A. 19, 2746.

7. Marqueyrol and Muraour, Mem. Poudres 21, 259 (1924).

8. Marqueyrol and Loriette, The Causes of Certain Phenomona Observed in the Course of the Manufacture of Powder, Mem. Poudres 21, 276-80 (1924), C.A. 19, 2746.

9. Davis and Ashdown, Transformations of Diphenylamine during the Aging of Smokeless Powder, Ind. Eng. Chem. 17, 674 (1925), C. A. 19, 2413.

10. Davis and Ashdown, Color Tests for Nitro Derivatives of Diphenylamine, J. A. C. 46, 1051-4 (1924).

11. F. Becker and G. A. Hunold, Diphenylamine in Smokeless Powder, z. ges. Schies-u Sprengstoffw., 33, 213-215 (1938), C. A. 32, 9501.

Table of Contents

1. [illegible] Chem.

2. [illegible] Chem.

3. [illegible] Chem.

4. [illegible] Chem.

5. [illegible] Chem.

6. [illegible] Chem.

7. [illegible] Chem.

8. [illegible] Chem.

9. [illegible] Chem. 17, 374 (1929); C. A. 17, 2413.

10. Davis and Baldwin, Color Tests for Nitro Derivatives of Diphenylamine, J. A. C. S. 46, 1091-4 (1924).

11. [illegible] and G. A. Mandin, Diphenylamine in Smokeless Powder, N. Gas. Sobleau-u Sprengstoffw., 32, 213-215 (1937), C. A. 32, 9501.

12. M. Labrey, Disengagement of Nitric Oxide from Nitro Products at Low Temperatures, Comp. Rendu. 205, 978-9 (1937) C. A. 32, 781

13. H. Muracour, Attack of Nitric Esters by Diphenylamine in the Presence of Catalysts, Bull. Soc. Chim. (5) 3, 2240-51 (1936) C. A. 31, 3697

14. Anon., Stability of Old Powders, Mem. Poudres 25, 472-5 (1932-3) C. A. 28, 5985

15. U. S. Patent 2, 123, 517, Smokeless Powder Stabilization, Richard G. Woodbridge (to E. I. Dupont) July 12, 1938

16. M. A. Apard, Nitro Derivatives of the Centralites, Mem Poudres 22, 180-90, (1926) C. A. 22, 166

17. H. Lecorche and P. L. Jovinet, Transformation Products of Centralite in Stored Smokeless Powders, Mem. Poudres, 23, 147-54 (1928) C. A. 23, 2296

18. U. S. Patent 2, 096,451 Triacetate of alkyl-trimethylol methane used as gelatinizer and stabilizer in nitro cellulose and nitroglycerine, P. P. Delfino, Oct. 19, 1937, C. A. 32, 357

19. Gina and Guastalla, Stabilizers and Gelatinizers in Smokeless Powders, Chimie and Industrie, 29, 268-77 (1933) C. A. 27, 2580

20. Mario Tonegutti, The Stabilizing Power of Various Compounds Studied Comparatively in the Taliana and Thomas Tests. Att. V. Congr. Nazl. Chim. Pura Applicata, Rome, 1935, Pt. II, 899-915 (1936) C. A. 31, 9198

12. [illegible], Dynamo-genesis of [illegible] oxide iron [illegible] [illegible]
[illegible] Iron Tonnes [illegible], [illegible], [illegible], 1936, [illegible]
(1937) [illegible]

13. [illegible], Effect of [illegible] [illegible] on [illegible] [illegible]
[illegible] [illegible] [illegible], [illegible], [illegible]
[illegible] (1936) [illegible], [illegible], 1937

14. [illegible], [illegible] of Oil [illegible], [illegible], [illegible]
(5 [illegible]) [illegible], [illegible], 1937

15. [illegible], [illegible], 1937, [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] (to [illegible], [illegible], [illegible])
[illegible] 72, 1938

16. [illegible], Nitro Derivatives of the [illegible], [illegible]
[illegible] 22, [illegible], 1936) [illegible], [illegible], 22, 1936

17. [illegible] and [illegible], Thermoforming [illegible] of
[illegible] in [illegible] [illegible] [illegible], [illegible]
[illegible], 23, [illegible] (1936) [illegible], 23, 1936

18. [illegible], [illegible], [illegible] [illegible] of [illegible]
[illegible] used as [illegible] and [illegible] in
[illegible] [illegible] [illegible], [illegible], [illegible],
[illegible], 16, 1937, [illegible], 32, 397

19. [illegible] and [illegible], [illegible] [illegible] in [illegible]
[illegible], [illegible] and [illegible], [illegible], 286-97
(1933) [illegible], 27, 2920

20. [illegible], The [illegible] of [illegible] [illegible]
[illegible] [illegible] in the [illegible] and [illegible]
[illegible], [illegible], [illegible], [illegible], [illegible], [illegible]
[illegible], 1932, [illegible], II, 099-015 (1936) [illegible], 31, 0198

21. Mario Tonegutti, Same as 20, Z. ges. Schies.-u. Sprengstoffw. 32, 300-5. C. A. 32, 1099

22. Mario Tonegutti, Influence of Various Kinds of Petrolatums on Stability of Smokeless Powders, Ann. Chim. Applicata, 22, 620-6 (1932) C. A. 27, 1176

23. R. Dalbert, Comparison of Nitroglycerine Powders Stabilized with Centralite and Diphenylamine or Carbazole, Mem. Poudres, 28, 147-55 (1938) C. A. 33, 7569

24. B. R. Dalbert, Triphenylamine as a Stabilizer for Powder, Mem. Poudres, 27, 117-26 (1937) C. A. 31, 8201

25. Krauz and Majrach. Mechanism of the Stabilizing Influence of Tartaric Acid on Smokeless Powders, Chem Obzor. 8, 213-4, 233-9 (1933) C. A. 28, 4907

26. Krauz and Majrach, The Nitro Esters of Polyhydroxy Dicarboxylic Acids, Collection Czech. Chem. Commun., 11, 639-48 (1939) C. A. 35, 2721

27. Desmaroux, The Ballistic Stability of Camphor and Centralite Powders, Mem. Poudres, 24, 282-4, (1930) C. A. 26, 5759.

28. G. C. Hale, Action of Diphenylamine in Smokeless Powder, Army Ordnance 5, 674-5 (1925) C. A. 19, 1056.

DATE DUE

AUG 31 BINDERY

Thesis 7945
P8 Prager
AUTHOR
Stabilization of
TITLE smokeless powder

DATE LOANED	BORROWER'S NAME	DATE RETURNED

of

Thesis 7945
P8 Prager
The stabilization of
smokeless powder.

Library
U. S. Naval Postgraduate School
Monterey, California

ARTISAN GOLD LETTERING AND SMITH BINDERY

thesP8
Stabilization of smokeless powder.
3 2768 001 93169 4
DUDLEY KNOX LIBRARY